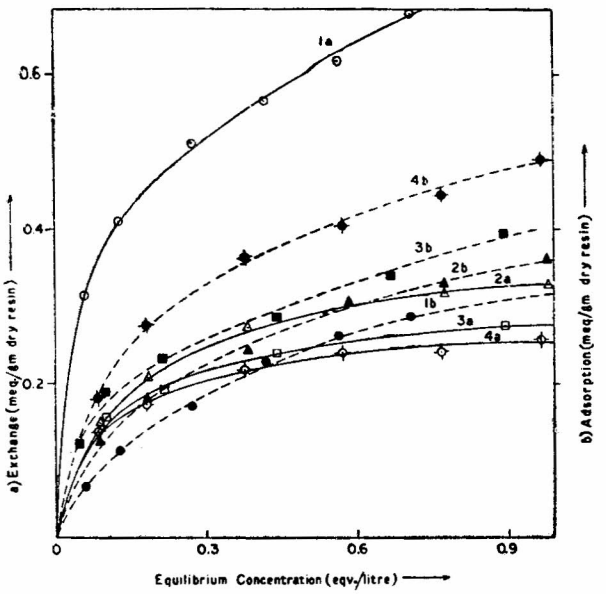

Fig. 1 — Ion exchange (a) and adsorption isotherms (b) of carboxylic acids on the K^+ form of Amberlite IR-120 [(1) Formic, (2) acetic, (3) propionic and (4) *n*-butyric acids]

and consequently ion exchange is lower. The dissociation constant[6] decreases with the chain length of the carboxylic acids, excepting in the case of *n*-butyric acid. The dissociation constant of *n*-butyric acid is higher than that of propionic acid. So, besides dissociation constant, chain length effect also plays an important role in adsorption as well as in ion exchange of the carboxylic acids. The dissociation constants of chloroacetic acids increase with the number of substituted chlorine atoms. Accordingly, adsorption decreases and ion exchange increases from mono- to trichloroacetic acid.

The behaviour of molecular adsorption and ion exchange of a particular acid with the three different salt forms of the resin are compared in Table 1.

From the Table 1 it is seen that, except in the case of formic acid, exchange of H^+ from the acids by the different salt forms of the resin follows the same order, e.g $R_2Mg < RK < RNa$. The exchanging powers of the ions with the hydrogen form of the cation-exchange resin increases in the order $Na^+ < K^+ < Mg^{2+}$. Naturally, the competing H^+ ion of the acids is exchanged for the above ions in the order $R_2Mg < RK < RNa$.

Table 1 — Order of Adsorption and Ion Exchange of Different Carboxylic Acids on Different Salt Forms of the Resin

Acids	Ion exchange	Adsorption
Formic	$R_2Mg < RNa < RK$	$RNa < R_2Mg < RK$
Acetic	$R_2Mg < RK < RNa$	$RNa < R_2Mg < RK$
Propionic	$R_2Mg < RK < RNa$	$R_2Mg < RNa < RK$
n-Butyric	$R_2Mg < RK < RNa$	$R_2Mg < RNa < RK$
Monochloroacetic	$R_2Mg < RK < RNa$	$RNa < R_2Mg < RK$
Dichloroacetic	$R_2Mg < RK < RNa$	$RNa \approx R_2Mg < RK$
Trichloroacetic	$R_2Mg < RK < RNa$	$RNa \approx R_2Mg < RK$

R = resin matrix.

It is expected that adsorption of the acids would be highest by the Mg^{2+} form of the resin and least by the Na^+ form. The anomalies, observed in the case of Mg^{2+} form, may be due to the formation of complex between Mg^{2+} and the carboxylate anions.

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Dissociation Constants of Substituted Benzoic Acids by Conductometric Methods

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The pK_a values of *p*-bromobenzoic acid and *p*-iodobenzoic acid in ethanol+water mixtures (8-76 wt % of ethanol) have been determined using conductometric method suggested by Gelb with modification. The results have been further verified by Fuoss and Kraus method. The role of solvents on the dissociation constants has been discussed.

In continuation of our studies[1-3] on the dissociation constants of weak acids by conductometric methods, we report in this note the dissociation constants of *p*-bromo- and *p*-iodobenzoic acids in ethanol-water mixtures by Gelb's[4] method.

The results have been further verified by the method due to Fuoss and Kraus[5,6].

Ethanol was purified and the weight-percentages and the relative permittivities of ethanol-water mixtures were determined as described before[1,7]. *p*-Bromo- and *p*-iodobenzoic acids (Purum, Fluka) were recrystallized from alcohol. The acids and $HClO_4$ (GR, Merck) were estimated volumetrically using NaOH (GR, Merck) standardized with succinic acid (GR, Merck) and potassium hydrogen phthalate (Baker analysed) in the usual way.

Conductance measurements were made at 25° ±0·02° using a Leeds-Northrup model 4959 conductance bridge with a sensitivity of ±0·1%. A 50-60 cycle signal was employed. A dip-type Philips conductance cell with cell constant $\theta = 0{\cdot}85$ cm^{-1} was utilized.

The dissociation constant of a weak acid in presence of completely dissociated $HClO_4$ is given by Eq. (1)

$$K = \frac{\alpha(\alpha C_{HA} + C_{HClO_4}) \times f_{\pm}^2}{(1-\alpha)} \qquad \ldots(1)$$

TABLE 1 — DISSOCIATION CONSTANTS OF *p*-BROMO- AND *p*-IODOBENZOIC ACIDS

EtOH (wt %)	Mole fr. of EtOH	Λ^0 (mhos cm²/eqv.)		pK_a of *p*-bromobenzoic acid			pK_a of *p*-iodobenzoic acid		
		p-Bromo	*p*-Iodo	(a)	(a)*	(b)	(a)	(a)*	(b)
0·0	0·000	384·0	385·2	3·95	3·98	3·98	3·95	3·99	4·00
8·0	0·033	347·5	346·0	4·10	4·15	4·17	4·05	4·11	4·11
16·4	0·071	284·9	282·8	4·30	4·36	4·38	4·24	4·29	4·31
25·3	0·117	232·1	229·4	4·50	4·55	4·57	4·41	4·50	4·54
34·4	0·170	180·9	179·4	4·80	4·88	4·87	4·74	4·84	4·82
44·0	0·235	144·4	146·9	4·92	5·02	5·05	4·90	5·02	5·05
54·1	0·315	126·8	130·1	5·22	5·32	5·35	5·27	5·36	5·39
64·7	0·418	97·6	96·8	5·46	5·58	5·63	5·52	5·59	5·63
76·0	0·556	75·1	76·0	5·76	5·87	5·92	5·79	5·90	5·97
87·6	0·740	—	—	—	—	6·27	—	—	6·35

(a) pK_a from the plot of ΛC vs $1/\Lambda$; (a)* pK_a from Fuoss and Kraus method; (b) pK_a from titration method.

The various terms in Eq. (1) have been defined earlier[3].

The refined values of α are obtained from Eq. (2)

$$\alpha = (C^*_{HClO_4} - C_{HClO_4})/\beta C_{HA} \quad \ldots(2)$$

when $\Lambda'_{HClO_4} = \Lambda'^*_{HClO_4}$ and $\beta = \Lambda'_{HA}/\Lambda'_{HClO}$.

β can be approximated to $\Lambda^0_{HA}/\Lambda^0_{HClO_4}$ at low concentrations of the acid and at low ionic strengths. These terms have been defined in an earlier paper[3]. $\Lambda^0_{HClO_4}$ values have been taken from our previous experiments and other details are the same as given before[1-3].

The initial values of Λ^0_{HA} and K of weak acids in mixed solvents were determined from the plot of ΛC against $\frac{1}{\Lambda}$ in the usual way. The refinement of Λ^0_{HA} and K values was made using the method of Fuoss and Kraus utilizing the relationship (3)

$$f(z)/\Lambda = \frac{1}{K\Lambda^{02}} \cdot \frac{\Lambda C f_\pm^2}{F(z)} + \frac{1}{\Lambda^{02}} \quad \ldots(3)$$

as described earlier[1-3,5,6].

The log $f_\pm$ values were calculated from Eq. (4)

$$-\log f_\pm = A\sqrt{\alpha C} \quad \ldots(4)$$

using the appropriate values of A.

The average values of Λ^0 and pK_a of substituted benzoic acids obtained by the two methods are given in Table 1. The results from the two methods agree fairly well. In spite of the limitations, Λ° values as given in the Table 1 seem to be quite in order. Λ° values decrease as the percentage of ethanol increases as usual[8].

It is also noted that the pK_a values when plotted against $1/\epsilon$ or mole-fraction give excellent linear plots up to 65 wt % ethanol in water. Deviations are noted at higher percentages of ethanol. Improvement is only marginal when water activities are taken into consideration.

From the results together with our values for the dissociation constants of benzoic and substituted benzoic acids reported earlier[2] it is apparent that Born equation[9] or modified equations[10-14] are unable to account for the variations of pK with the dielectric constant.

Ohtaki[15] has shown that the variation of pK for charged acids in ethanol-water mixtures can be accounted for by combining the Born equation with terms which depend upon a knowledge of hydronium-alkoxonium ion equilibria in the solvent mixtures.

The treatment gives the equation

$$[pK(s) - pK(w)]_R - [pK(s) - pK(w)]_O = 121{\cdot}6\left(\frac{1}{\epsilon} - 0{\cdot}0128\right)\left(\frac{1}{r_{A_R}} - \frac{1}{r_{A_O}}\right) \quad \ldots(5)$$

for comparison of medium effects for two charged acids.

The equation has the advantage that it cancels the term due to free energy of transfer of H^+ ions which is a complicated function of solvent mixture and not a linear function of $1/\epsilon$. But the relationship fails and the treatment does not help much for the comparison of the relative behaviour of pair of acids as observed by Rochester[16].

The $\Delta pK_a[=(pK_s - pK_w)]$ values or "medium effects" of all these acids are almost the same within limits of experimental accuracy. A slight variation may arise due to structural modification of solvation shells due to a change in the ratios of water in the solvation shells of anions having polar substituents.

From the results, it is clear that the knowledge of 'non-electrostatic' contributions resulting from ion-solvent interactions, solvent-basicity, etc., are necessary to explain the variations of pK with solvents.

Lastly, we emphasize the need of determining the dissociation constants of weak acids by conductometric methods with accurate bridges to evolve a suitable and unambiguous method of determination of dissociation constants in mixed solvents.

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Dissociation Constants of Glycine, Alanine, Proline, Valine, Glutamine & γ-Aminobutyric Acid in Methanol & Ethanol-Water Mixtures

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The ionisation constants of glycine, alanine, proline, valine, glutamine and γ-aminobutyric acid have been determined *p*H-metrically in ethanol-water and methanol-water mixtures at very low ionic strengths and at 25°.

THE effect of non-aqueous solvents on the dissociation constants of acids and bases is not well understood, even though the advantages and utility of non-aqueous and mixed solvents for improving analytical methods involving complexation have been well-emphasized[1]. The literature[2] provides numerous studies on the dissociation constants of carboxylic acids. However, comparatively little is known regarding the effect of solvents on the dissociation of amino acids.

In view of these facts, we have undertaken studies on the protonation equilibria of a number of amino acids like glycine, alanine, proline, valine, glutamine and γ-aminobutyric acids in methanol and ethanol water mixtures *p*H-metrically. The choice of the present solvent systems was dictated by the nature of the protolytic behaviour of the amino acids closely resembling water yet differing much in physical properties.

The amino acids (except GR E. Merck variety) were purified by crystallization from water-ethanol mixtures. Methanol and ethanol were purified and the weight percentages of the organic solvent were determined in the same way as described before[3,4]. The slight traces of water present, if any, in the organic solvents were neglected.

Perchloric acid and caustic soda were of E. Merck reagent grade and were standardized in the usual way. Other chemicals were of reagent grade. All the solutions were made in doubly distilled water.

For the determination of the acid dissociation of dipolar ions, a known concentration of the amino acid was neutralized to different extents with perchloric acid and the hydrogen ion concentration measured. The process was repeated with different concentrations of the different dipolar ions in various methanol-water and ethanol-water mixtures.

For the determination of the second dissociation of the amino acids, the process was the same; only $HClO_4$ was replaced by caustic soda.

The *p*H-meter readings were taken at 25° using a Cambridge bench type battery operated *p*H-meter.

Since the amino acids are present predominantly as dipolar ions (i.e. $^{+}NH_3RCO_2^{-}$), these are represented as $RH^{\pm}$ and the dissociation equilibria in acid (if dissociation of carboxylic group is considered) and alkali (if dissociation ammonium ion is considered) can be represented by Eqs. (1) and (2).

$$RH_2^{+}+H_2O \rightleftharpoons H_3O^{+}+RH^{\pm},\ K_1=\frac{a_{H^+}\times a_{RH^{\pm}}}{a_{RH_2^+}} \quad \ldots(1)$$

$$RH^{\pm}+H_2O \rightleftharpoons H_3O^{+}+R^{-},\ K_2=\frac{a_{H^+}\times a_{R^-}}{a_{RH^{\pm}}} \quad \ldots(2)$$

or

$$pK_1 = p\text{H}-\log\frac{C_{RH^{\pm}}}{C_{RH_2^+}}-\log\frac{f_{RH^{\pm}}}{f_{RH_2^+}}$$

$$= p\text{H}-\log\left(\frac{C}{a-C_{H^+}}-1\right)-\log\frac{f_{RH^{\pm}}}{f_{RH_2^+}}$$

and

$$pK_2 = p\text{H}+\log\left(\frac{C}{b-C_{OH^-}}-1\right)-\log\frac{f_{R^-}}{f_{RH^{\pm}}}$$

where C = concentration of neutral amino acid, a or b = concentration of acid or base respectively, and C_H^+ or C_{OH^-} = concentration of H^+ ion or OH^- ion in the experimental solution (determined *p*H-metrically). The appropriate corrections were made for the mixed solvents using the well known method described earlier[5-7]. Though the 'correction factors' for the mixed solvents were known[7], we considered it desirable to find out the 'correction factor' with each set of measurement to avoid any error resulting from (i) change in the asymmetry potential of the glass electrode and (ii) liquid-junction potential of uncertain magnitude.

Since the ionic strengths of the solutions were very low ($3\text{-}6\times10^{-3}M$) activity coefficients were approximated to unity.

The method is almost similar to that of Edsall and Blanchard[8].

The pK_1 and pK_2 values at 25° determined in different percentages of methanol-water and ethanol-water mixtures are presented in Table 1. The results are in very good agreement with the reported values for glycine and alanine in ethanol-water mixture determined potentiometrically by Edsall and Blanchard[8].

As expected, pK_1 values of all the amino acids increase with increase in the alcohol content of the mixtures but the magnitude of increase is smaller than that of corresponding carboxylic acid due to 'dipolar character' of the acids.

The pK_1 values were found to be linear function of $1/\epsilon$ and mole-fraction of alcohol at low percentages of alcohol. Slight improvement was observed when water activity was taken into consideration[9]. It is to be noted that the proportion of the neutral form of acid increases[8] with increase in alcohol content resulting in deviations.